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Synthesis, Characterization and Visible Light Degradation of Organic dye by Chemically Synthesized ZnO/γ-Fe_2O_3 Nanocomposites

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ABSTRACT: In the present study ZnO/γ-Fe_2O_3 nanocomposites is prepared by the simple co-precipitation method. The prepared composites materials were characterized by X-ray diffraction (XRD), high resolution scanning electron microscope (HRSEM), energy dispersive X-ray spectroscopy (EDX), Brunauer Emmett Teller analysis (BET), and UV-visible spectroscopy. XRD confirmed the formation of hexagonal wurtzite nature of ZnO and cubic structure of γ-Fe_2O_3 in the composite materials, while SEM images shown spherical and rod like structure. BET analysis confirmed the mesoporous behavior of nanocomposites. UV-Visible spectroscopy has been applied to the measurement of band gap and photo-oxidation behavior of organic dye methyl blue and rhodamine B (Rh B). Experimental data suggested that ZnO/γ-Fe_2O_3 nanoparticles catalyst possessed the highest catalytic activity towards Rh B degradation in aqueous solution as comparison to the methylene blue at the tested concentration level of 1×10^{-5} M.

KEYWORDS: Nanocomposites, XRD, HRSEM, EDX, BET.

I. INTRODUCTION

Over the last several decades semiconductor materials such as photocatalysis has been intensively explored in the vision of its prospective properties towards the remediation of environmental contaminants and treatment of waste water [1]. Generally, semiconductors materials such as ZnO, TiO_2, SnO_2 etc. are UV light consuming photocatalyst and concerned as remarkable devotion from the scientists [2-4]. Chakrabarti and Hong reported that ZnO is investigated to be a superior photocatalyst than TiO_2 in the photocatalytic degradation of organic contaminants in the presence of UV and visible light irradiations [5, 6]. Zinc oxide (ZnO) is a low cost chemically stable and environmentally nontoxic n-type semiconductor material having a large band gap of 3.37 eV with a large excitation binding energy of 60 meV at room temperature which can be investigated to be a possible pathway in dye-sensitized solar cells and photocatalysis [7] because of its strong metal support interaction (SMSI) properties. The exposer of UV light on ZnO semiconductor material, it has the capability to produced oxidative species like as hydroxyl radicals (•OH) and superoxide anions ($O^{2\bullet-}$), which display oxidative properties robust enough to oxidize certain organic contaminants. Consequently, to increase the photocatalytic proficiency and stability, it is of fundamental importance to quash the recombination of electron-hole pairs of ZnO. However, due to the wide band gap of ZnO materials their light absorption only in the UV spectral region of the solar spectrum and limits expenses of solar energy thus limits efficiency in sunlight. However, the improvement of photocatalytic activity of ZnO nanoparticles, under visible light radiation is highly desired. As comparison with a single semiconductor, photocatalysis compelled by composite semiconductors is also extensively studied to improve the photocatalytic activity in the visible region [8]. In the present period of time many researchers are synthesize numerous type of zinc oxide nanocomposites like as ZnO/metal, ZnO/metal oxide and ZnO/polymer and doped with transition metals and non-metals to reduce the band gap and display visible light photocatalysis, because of the presence of intermediate states in the nanocomposite which engages visible light that stimulates electrons and holes in the photo reaction [9, 10]. Reddy et al. fabricated ZnO:RGO/RuO_2 nanocomposites with outstanding degradation efficacy of methylene blue underneath simulated sunlight [11]. Eskizeybek et al. described photo degradation of organic dye malachite green (MG) and methylene blue in the presence of ordinary sunlight by adopting a

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polyaniline:ZnO nanocomposite [12]. And Saravanan, et al. described that superior degradation of methyl orange and methylene blue under visible light condition by of polyaniline (PANI)/ZnO nanocomposite system [13].
Hence, the present work is mainly concentrated on the simple fabrication of $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposites by chemical co-precipitation method and examination its catalytic activities were investigated for the photo-degradation of a model organic dye rhodamine B and methylene blue under visible light irradiations. The synthesized nanocomposites materials were characterized by Powder XRD, UV-vis, HRSEM, BET, and EDAX. The photo degraded samples were analyzed by UV-Visible spectroscopy.

II. EXPERIMENTAL SECTION

A. CHEMICAL AND MATERIALS

All the required chemical reagent are analytical grade as zinc (II) sulphate heptahydrate ($ZnSO_4.8H_2O$), Iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$), Rhodamine B and methylene blue was purchased from Merck India, sodium hydroxide (NaOH) powder was purchased from MP Biomedical LLC India and used without further purification. Double de-ionized water was used as solvents. All the glassware's were cleaned and rinsed by concentrated acid. The dried glassware's were used in all the experiments.

B. SYNTHESIS OF ZINC OXIDE- IRON OXIDE ($ZnO/\gamma\text{-}Fe_2O_3$) NANOCOMPOSITES

The nanorod and nano-spherical mixed like $ZnO/\gamma\text{-}Fe_2O_3$ was synthesized from its precursor through a simple chemical co-precipitation method. In the typical synthesis process 25 ml of 0.5 mole $ZnSO_4.8H_2O$ and 25 ml of 0.5 mole of $FeSO_4.7H_2O$ solution were mixed and stirred on the magnetic stirrer for 30 min, clear solution obtained. The obtained clear solutions were placed in an ultrasonic cleaner operating at 57 kHz for 2 h. After the completion of sonication the mixed solutions were continuously again stirred for 30 min then a suitable amount of NaOH solution in an obtained aqueous solution was added to the mixed solutions until a pH of 12 was reached. The resulting reaction mixture was stirred for 30 min, and then it was allowed to aging at room temperature for 18 h. Next, the solution was centrifuged and washed several times with ethanol and distilled water and finally with acetone to remove unwanted impurities. The final product was dried in a muffle oven at 200 ^{o}C for 1 h yielding the brown $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposites powder.

C. CHARACTERIZATION

The vastly visible light dynamic nanocatalyst was synthesized by a simple chemical co-precipitation method and characterized by powder X-ray diffraction (XRD), Ultraviolet-visible spectroscopy (UV-Vis), High Resolution Scanning Electron Microscope (HR-SEM), Energy Dispersive X-ray Spectroscopy (EDAX), and Brunauer-Emmett-Teller (BET) surface area investigation was accompanied by using the nitrogen absorption-desorption measurement at 77 K (BELSORD mini, Japan). The photocatalytic ability of the prepared materials was examined using Rhodamine B and methylene blue organic dye pollutants. The measurement of the photo-degradation ability of the catalyst was estimated by using UV-Vis spectroscopy (Carry 100).

D. STUDY OF PHOTOCATALYTIC ACTIVITY

The application of the synthesized materials was concluded by photo-degradation of Rhodamine B and methylene blue in presence of visible light radiation in a photocatalytic chamber. 20 mg quantity of prepared $ZnO/\gamma\text{-}Fe_2O_3$ catalyst was initially dissolve in 100 ml of 1×10^{-5} M, Rhodamine B and methylene blue standard solution and mixture of the solution was stirred for 30 min in the dark condition in order to attaining the adsorption-desorption equilibrium. Finally the solution was irradiated with visible light from the fluorescent lamp (9W) in a photocatalytic chamber. The solution was agitated, during irradiation by using a magnetic stirrer and air was supply into the reaction mixture to implement a constant supply of oxygen. After the preferred time interval, an aliquot amount of the solution was withdrawn, centrifuged and take its absorbance on UV-visible spectrophotometer to measure the percentage degradation. The degradation efficiency of photocatalytic was measured by applied the following equation:

$$(\%)\,\text{degradation} = \left\{ \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \right\}$$

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Where A_0 represents the initial absorbance of the dye solution and A_t; the absorbance after irradiation at a particular time t.

III. RESULT AND DISCUSSION

A. XRD ANALYSIS

XRD patterns of the ZnO/γ-Fe_2O_3 nanocomposites materials are shown in Fig. 1. A series of characteristic peaks 31.76, 34.40, 36.24, 47.61, 56.61, 62.89, 66.41, 67.93 and 69.72, which are corresponds to the Miller indices (100), (002), (101), (102), (110), (103), (200), (112) and (201) were observed and they were in accordance with wurtzite phase (JCPDS no. 76-0704) of ZnO, presence of other peaks at 18.31, 30.10, and 43.12 correspond to the Miller indices (111), (220) and (400) planes of γ-Fe_2O_3 phase with cubic phase (JCPDS no. 85-1436) indicate that the above material is ZnO/γ-Fe_2O_3 composite. The average particle sizes (94 nm) of ZnO/γ-Fe_2O_3 were calculated using Scherrer's Eq. (1):

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where λ denotes the wavelength of the radiation equal to 0.154 nm, β is the full width at half maximum and θ is the half diffraction angle.

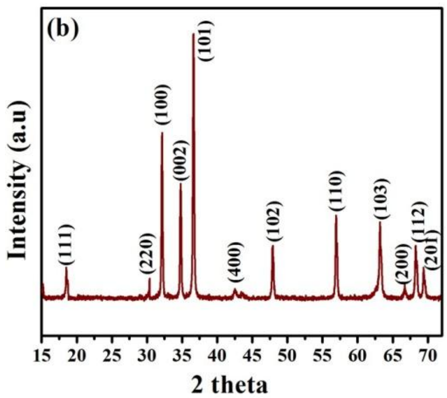

Figure 1 XRD pattern of ZnO/γ-Fe_2O_3 composite

B. SEM IMAGE ANALYSIS

HR-SEM images of ZnO/γ-Fe_2O_3 nanocomposites are shown in Fig. 2 (a). HR-SEM images which shows the morphology of the prepared nanocomposites material. It display that the more nanocomposites material carry a uniform spherical and some rod-like structure in the morphology and the size of the particles are in nano ranged. A closer examination reveals that these nano-spherical are actually composed of small ZnO nanoparticles leading to a relatively rough surface.

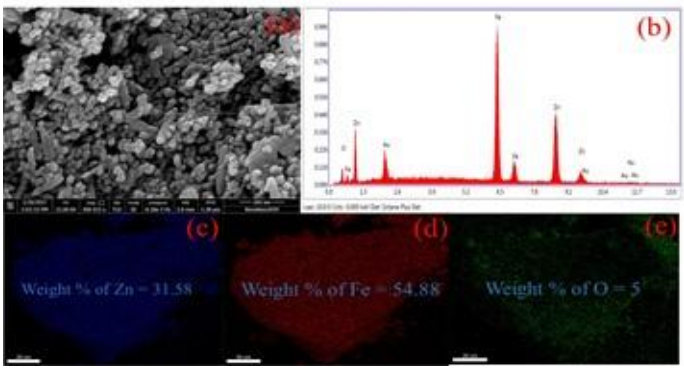

Figure 2 (a) HRSEM image (b) EDX spectra (c-e) X-ray elemental mapping of ZnO/γ-Fe_2O_3 composite

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A comprehensive chemical composition analysis of the nanomaterial was carried out with energy dispersive spectroscopy (EDS) and elemental mapping Fig. 2 (b-e) shows the presence of 54.88 wt% of Fe, 31.58 wt% of Zn and 5 wt% of O in the EDS spectrum. The presence of Fe, Zn, and O specified the production of the $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposite. The elemental mapping (area) achieved from EDS analyses display that Fe, Zn, and O are homogeneously dispersed in the $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposite. The point EDX investigation also specifies the presence of Fe, Zn, and O in the materials, which again validates the homogeneous composition of the nanocomposite.

C. BET ANALYSIS

The surface properties of $ZnO/\gamma\text{-}Fe_2O_3$ catalyst were investigated by using BET surface area analyzer to calculate the surface area of the samples. Fig 4 shows the isotherms of N2 adsorption-desorption have been used to determine surface area of $ZnO/\gamma\text{-}Fe_2O_3$ material at liquid nitrogen temperature and the Barret-Joyner-Halenda (BJH) method was used to evaluate the pore size distribution. The pore size distribution curve indicates that pores are mainly two type and their size lies in mesoporous range. Hysteresis is observed as a result of pore filling and emptying processes occurring separately, as shown in Fig. 4. N2 adsorption-desorption isotherm display a Type IV hysteresis [14], characteristic of mesoporous materials with a H2 type hysteresis loop [15] typical for non-uniform shape and size of pore channels being fully consistent with the HR-SEM data. From BET evaluation of $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposites surface area is calculated 50.54 $m^2\ g^{-1}$.

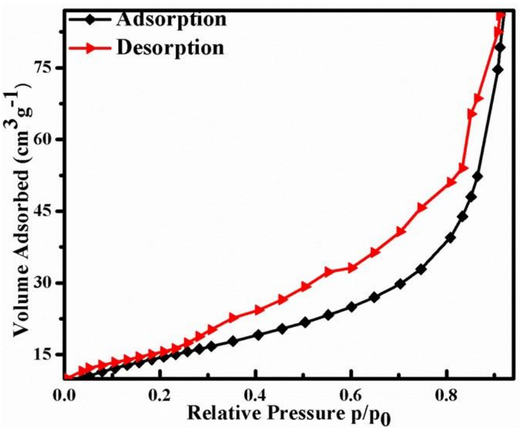

Figure 3 Adsorption- Desorption plot of $ZnO/\gamma\text{-}Fe_2O_3$ composite

D. OPTICAL PROPERTIES

A little amount of synthesized sample (in milligrams) is dissolved in deionized water (3 ml) and sonicate until a clear solution is obtained. The UV-Vis spectra is taken for the examination of the optical properties of $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposites materials. Fig. 5 demonstrate the UV-Vis diffuse reflectance spectra of the $ZnO/\gamma\text{-}Fe_2O_3$ composite. On the formation of $ZnO/\gamma\text{-}Fe_2O_3$ composite the wavelength absorption edge from 373 nm to 434 nm. Measurement of UV-Vis spectroscopy were applied for the calculation of direct band gaps of $ZnO/\gamma\text{-}Fe_2O_3$ with the following equation [16]:

$$Eg = 1239.8/\lambda$$

Where Eg is the band gap (eV) and λ is the wavelength (nm) of the absorption edges in the spectrum. Band gap energy of $ZnO/\gamma\text{-}Fe_2O_3$ nanocomposites is calculated to be 2.85 eV.

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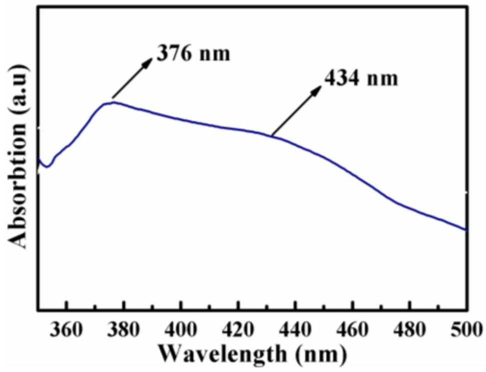

Figure 4 UV-Visible Spectrum of $ZnO/\gamma-Fe_2O_3$ composite

IV. PHOTOCATALYTIC ACTIVITY

The photo degradation application of organic pollutants by the prepared $ZnO/\gamma-Fe_2O_3$ photo catalysts was considered by measuring photo degradation performance with their corresponding time dependent of methyl blue (MB) and rhodamine B (Rh B) in the presence of visible sun light shown in fig. 5. The degradation efficiency and rate of catalysis are surface area dependent phenomena since electron hole pair transfer occurs at the surface [17]. BET surface area is used to estimate the surface properties as it holds a great significance in case of adsorption, heterogeneous catalysis reactions on material surfaces. The dye degradation is estimated in terms of the change in absorption at λ_{max} = 668 nm for methylene blue and λ_{max} = 544 nm for rhodamine B dye respectively. The degradation efficiency is calculated to be 30 % for the methylene blue and 50 % for rhodamine B.

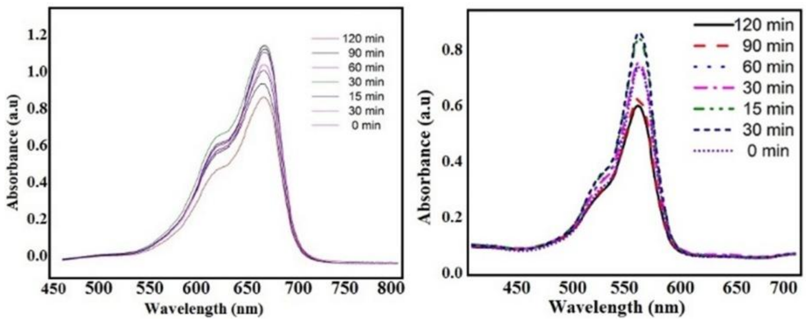

Figure 5 photocatalytic degradation of (a) methylene blue and (b) rhodamine B organic dye.

V. CONCLUSION

In the current experiment, we have fabricated $ZnO/\gamma-Fe_2O_3$ composite by chemical method. The prepared material was characterized by using X-ray diffraction, HRSEM, BET, and UV-Visible analysis. The size of the ZnO/ $\gamma-Fe_2O_3$ materials is uniform in size and particle sizes calculated to be 94 nm by X-ray diffraction analysis. Spherical and rod-like structure of ZnO/ $\gamma-Fe_2O_3$ composite was recognized by SEM analysis. The coupled semiconductor composite material ZnO/ $\gamma-Fe_2O_3$ shown more photocatalytic degradation of rhodamine B as comparison to the methylene blue in the visible sun light irradiation.

REFERENCES

[1] Liu, G. Zhao, Y. Sun, C. Li, F. Lu, G.Q. Cheng, H.M. 2008. Synergistic effects of B/N doping on the visible-light photocatalytic activity of mesoporous TiO_2. Angewandte Chemie International Edition. 47: 4516-4520.

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International Journal of Advanced Research in Science, Engineering and Technology
Vol. 4, Issue 5 , May 2017

[2] Jiang, X. Wang, T. 2007. Influence of preparation method on morphology and photocatalysis activity of nanostructured TiO_2. Environmental science & technology. 41: 4441-4446.
[3] Becker, J. Raghupathi, K.R. St. Pierre, J. Zhao, D. Koodali, R.T. 2011. Tuning of the crystallite and particle sizes of ZnO nanocrystalline materials in solvothermal synthesis and their photocatalytic activity for dye degradation. J. Phys. Chem. C. 115: 13844-13850.
[4] Sinha, A.K. Pradhan, M. Sarkar, S. Pal, T. 2013. Large-scale solid-state synthesis of Sn-SnO_2 nanoparticles from layered SnO by sunlight: a material for dye degradation in water by photocatalytic reaction. Environmental science & technology. 47: 2339-2345.
[5] Chakrabarti, S. Dutta, B.K. 2004. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. J. hazard mater. 112: 269-278.
[6] Hong, R. Pan, T. Qian, J. Li, H. 2006. Synthesis and surface modification of ZnO nanoparticles. Chem. Eng. J. 119: 71-81.
[7] Chu, D. Masuda, Y. Ohji, T. Kato, K. 2009. Formation and photocatalytic application of ZnO nanotubes using aqueous solution. Langmuir. 26: 2811-2815.
[8] Choi, J. Park, H. Hoffmann, M.R. 2009. Effects of single metal-ion doping on the visible-light photoreactivity of TiO_2. J. Phys. Chem. C. 114: 783-792.
[9] Yu, Q. Li, J. Li, H. Wang, Q. Cheng, S. Li, L. 2012. Fabrication, structure, and photocatalytic activities of boron-doped ZnO nanorods hydrothermally grown on CVD diamond film. Chem. Phys. Lett. 539: 74-78.
[10] Saravanan, R. Khan, M.M. Gupta, V.K. Mosquera, E. Gracia, F. Narayanan, V. Stephen, A. 2015. ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents. J. Colloid Interface Sci. 452: 126-133.
[11] Reddy, D.A. Ma, R. Kim, T.K. 2015. Efficient photocatalytic degradation of methylene blue by heterostructured ZnO–RGO/RuO_2 nanocomposite under the simulated sunlight irradiation. Ceram. Int. 41: 6999-7009.
[12] Eskizeybek, V. Sarı, F. Gülce, H. Gülce, A. Avcı, A. 2012. Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations. Appl. Catal., B. 119: 197-206.
[13] Saravanan, R. Sacari, E. Gracia, F. Khan, M.M. Mosquera, E. Gupta, V.K. 2016. Conducting PANI stimulated ZnO system for visible light photocatalytic degradation of coloured dyes. J. Mol. Liq. 221: 1029-1033.
[14] Sharma, N. Jha, R. Baghel, S. Sharma, D. 2017. Study on photocatalyst Zinc Oxide annealed at different temperatures for photodegradation of Eosin Y dye. J. Alloys Compd. 695: 270-279.
[15] Sing, K. 2001. The use of nitrogen adsorption for the characterisation of porous materials. Colloids Surf., A. 187: 3-9.
[16] Mohamed, R.M. McKinney, D. Kadi, M.W. Mkhalid, I.A. Sigmund, W. 2016. Platinum/zinc oxide nanoparticles: Enhanced photocatalysts degrade malachite green dye under visible light conditions. Ceram. Int. 42: 9375-9381.
[17] Wang, H. Li, G. Jia, L. Wang, G. Tang, C. 2008. Controllable preferential-etching synthesis and photocatalytic activity of porous ZnO nanotubes, J. Phys. Chem. C. 112: 11738-11743.